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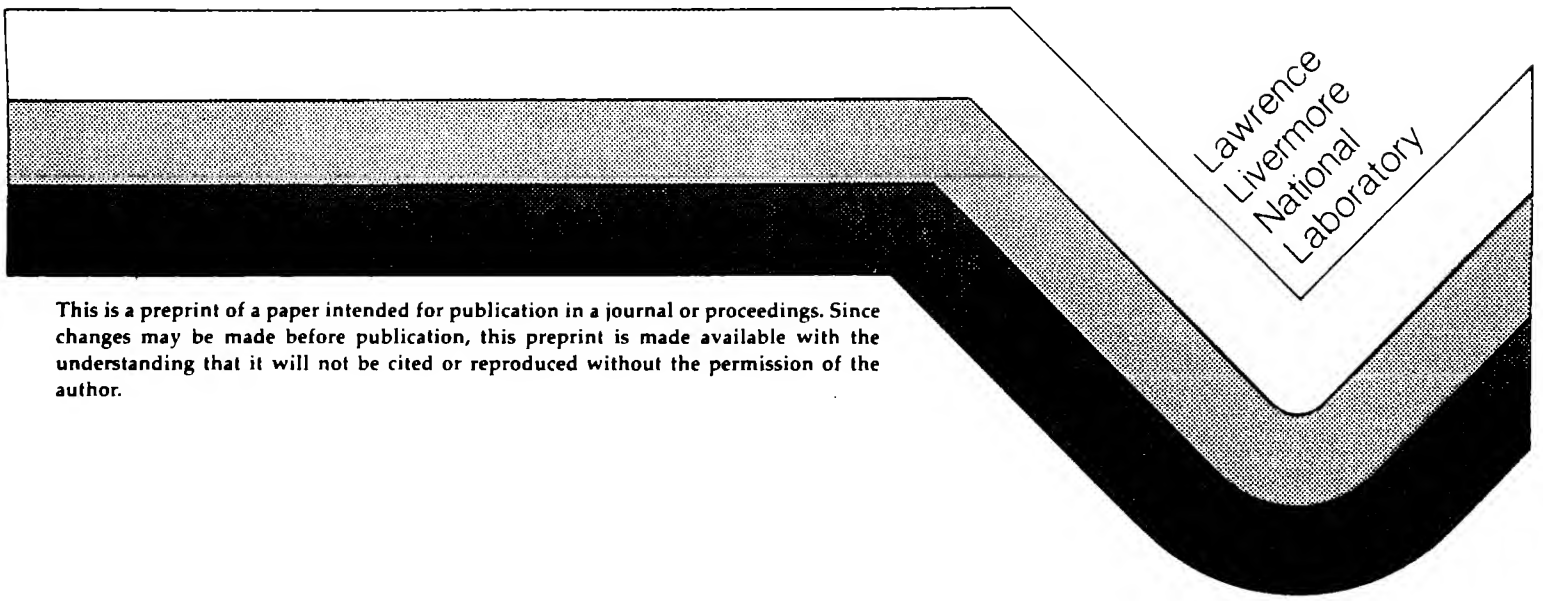

# THE SEARCH FOR HIGH ENERGY LOW VULNERABILITY EXPLOSIVES*

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## ABSTRACT

Lawrence Livermore National Laboratory (LLNL) is currently attempting to formulate explosives which have approximately 30% greater energy than our current TATB/Kel-F explosive, while still passing the Department of Energy's (DOE) Insensitive High Explosive (IHE) criteria. The new formulations are comprised of HMX, TATB, and high density fluoropolymers and fluoroplasticizers. Variables in the study include the particle size of HMX, type of TATB (wet or dry aminated), the ratios of polymers to plasticizers, and formulation techniques. Initial small scale sensitivity tests and thermal testing have shown promising results. This paper will relate the up-to-date status of the project.

## Introduction

The current IHE (Insensitive High Explosives) predominantly used by LLNL (Lawrence Livermore National Laboratory) is LX-17, which is 92.5% TATB and 7.5% Kel-F 800. In the late seventies, a program called Safe High Energy Explosives (SHEE) was initiated at LLNL to attempt to formulate new explosives with higher energy than LX-17, while significantly decreasing the vulnerability relative to HMX based HE's. We hoped to accomplish this task by combining the safety of TATB with the energy of HMX. The result of this study was the RX-26 series of explosives, which is a family of explosives predominantly containing HMX, TATB, and low density polymers (nominally 48.5/45/6.5 volume percent, respectively).[1] Varying particle sizes of HMX were used, although Class E and LX-04 grade were studied the most (nominally 10 and 60 micron medians, respectively). During this study, no real effect of the difference in particle size was noted. Many different binders were used, the most common being Estane 5702-F1, Kel-F 800, Kraton G-1650, and Viton A.[2] The TATB used was wet animated. One of the more well known explosives in the DOE (Department of Energy) community developed in this study was RX-26-AF, which is comprised of HMX (Class E), TATB, and Estane (48.5/45/6.5 volume percent, respectively).

Generically speaking, the results of the SHEE effort are as follows. The formulations met the energy criteria set forth. While the energy was linearly dependent upon the HMX concentra-

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tion, the safety properties were not. These explosives were insensitive to some hostile stimuli. Specifically, in Susan and rifle bullet tests, the reactions were mild, and had a high threshold, similar to TATB/binder formulations.[3] Thermally, the SHEE explosives had thresholds similar to HMX/binder compositions, but the reactions were mild (more closely resembling a TATB based explosive). However, these materials were more like HMX based explosives in shock initiation responses. They would not pass current IHE criteria.

Our current effort will hopefully reduce the vulnerability by reducing the void volume, and also lowering the modulus of the system by the addition of plasticizer to the binder. This new effort has been named HERS (for High Energy Reduced Sensitivity). HERS will take the information gained in the SHEE program and add the following elements.

First, from work done at LLNL by R. Simpson etal, we know that shock initiation is strongly dependent upon the particle size of HMX.[4] Fine particle HMX will decrease the potential ignition sites, or "hot spots", both in size (intergranular) and quantity (intragranular), thereby decreasing shock ignitiability. We also know that when you are unable to press to high percentages of theoretical maximum density (TMD), you create void volume which can serve as hot spots. Since very fine particles are often difficult to process, we will experiment between a six micron median fluid energy mill ground HMX, which has been used successfully at LLNL in Extrusion Cast Explosive (ECX)[3] formulations, and LX-04 grade (sixty micron median) HMX.

Second, we will use both wet and dry aminated TATB. We know that wet aminated TATB has a smaller particle size distribution, and is therefore less sensitive to shock initiation. However, the larger particle size of the dry aminated TATB may exhibit a better packing function when combined with the six micron HMX, which may result in a higher percentage of TMD in pressed billets. In addition, we have also seen that the type of TATB and the binder selected, as well as its processing conditions, will affect the amount of growth the final explosive will undergo. With many binders, TATB exhibits an irreversible dimensional growth with thermal cycling within the normal stockpile to target sequence (STS). This can exceed 2 volume percent with 30 cycles from -54 to +74°C. For these reasons, we will experiment with both types of TATB to see which gives us the best overall properties.

Third, to produce an rubbery formulation, we will be using plasticized polymers as binders. The requirements for the binder system are overall high density, high molecular weight plasticizer, and a glass transition temperature ($T_g$) less than -54C. Since metal acceleration is strongly dependent upon the initial energy density of the HE, a high density binder will allow the use of more binder without immediately compromising performance. The high molecular weight plasticizer will provide a tough rubbery system, while the low $T_g$ will help to avoid any

crystallinity which could adversely affect low temperature properties.

## Experimental Results

TIGER, a computer code which models the chemistry of detonations and can predict the performance of explosives,[5] was used to determine a starting point for the compositions of these new formulations. As a reference, TIGER shows that RX-26-AF gives approximately 23% higher energy than LX-17. Using different binders and different densities, we could see that new formulations comprised of 50 volume percent HMX, 40 volume percent TATB, and 10 percent high density binder would yield anywhere from 22 to 25% more energy than LX-17. We decided that although this was slightly less than the goal of 30%, it would give us a good starting point.

After a large search for high density polymers and plasticizers which would possibly satisfy our criteria was conducted, our initial experimentation involved determining which materials were compatible, and then what levels of plasticization we could achieve with those systems. The goal is to obtain as high a plasticizer loading as possible, to reduce the modulus and pressed void volume. The binder candidates we looked at are shown in Table 1. The binder systems we are currently scaling up are Viton GF/Viton LM (1/0.7), Viton GF/Halocarbon Oil 1.8 (1/0.9), Eypel F/Viton LM (1/0.5), and Kel-F 800/Halocarbon Oil 1.8 (1/0.7) (ratios given are volume ratios). We are currently testing these binder systems to insure that no exudation will occur. We are doing this by exposing thin films of the binder systems, as well as pressed pellets of the actual explosive compositions, to a thermal cycle which runs from -54 to +74C, at a rate of two cycles per day.

**Table 1 - Binder Candidates**

| Polymers | Plasticizers |
|---|---|
| Eypel F (Ethyl Corp., 1.91) | Fluorolube Oil MO 10 (Occidental, 1.895) |
| Kel-F 800 (3M, 2.02) | Halocarbon Oil 1.8 (Halocarbon, 1.82) |
| Kel-F 3700 (3M, 1.85) | Viton LM (DuPont, 1.72) |
| Kynar 461 (Pennwalt, 1.76) | |
| Viton C-10 (DuPont, 1.82) | |
| Viton GF (DuPont, 1.91) | |

The above items are listed as: Product (Company, Density in g/cc). See Ref. 2 for descriptions of the Kel-Fs and Vitons. Eypel F is a poly(fluoroalkoxyphosphazene). Kynar 461 is a poly(vinylidine fluoride). The Fluorolube and Halocarbon Oils are oligimers of Kel-F.

Our preliminary formulations work included varying the processing methods, in addition to varying the type and particle size of explosive. Our first mixes were done using a dry paste

method, which is done in the vertical high shear mixers under heated jacket and air sweep operation. The products from this method were powders. We then tried slurry coating the formulations, varying the solvents that were used for the binder lacquers. We used the direct slurry process, which is defined as follows. Water is placed into a Holston reactor, which is then heated. The dry explosive is added to the water. A lacquer of the polymer and plasticizer is made, using such solvents as n-butyl acetate and methyl isobutyl ketone. This lacquer is added to the reactor. This immediately creates two phases, one of water and the other of all the other ingredients. The two phase mixture is vigorously agitated while the warm water and heated jacket begin to drive off the solvent. As the solvent leaves the system, the binder deposits itself on the crystalline explosive and the vigorous agitation ensures a homogenous blend of ingredients. As the solvent is driven off the tendency for the mass to coalesce is reduced and eventually it breaks up into small beads approximately one to three millimeters in size.

We tested our products at various stages of the scale-up, to insure that the small scale safety properties were satisfactory, and that they were not changing as the materials were scaled up. The average results for the new formulations are listed in Table 2, along with comparative data. We have chosen to discontinue the work done using the dry paste method, since the slurry method produces free flowing beads which are dust free. Also, while there was not a significant difference, it appeared that the materials made with the slurry method had slightly better safety properties. This may be because the explosives were better coated by the binder with that method.

**Table 2. SMALL SCALE SENSITIVITY TESTS**

| | HMX | RX-26-AF | Avg. of new HERS | TATB |
|---|---|---|---|---|
| Drop Hammer, cm | 35 | 108 | 150 | >177 |
| Electrostatic Spark | 1/10 @ .3J | 0/10 @ 1J | 0/10 @ 1J | 0/10 @ 1J |
| Chemical Reactivity Test,* cc/g | 0.01 | 0.32 | 0.15 | 0.02 |
| DSC, onset of exo | 250°C | 250°C | 275°C | 340°C |

* Amount of gas evolved per gram of explosive after being held at 120°C for 22 hrs.

We also did some mechanical pressings to get a rough idea of how well the materials would press. We were able to get almost all of the formulations to approximately 98% TMD in our small one-half inch press. The pellets were pressed at 30,000 psi, at temperatures of 60, 80, and 105C. We were encouraged by these results. Later work (when we scale-up further) will involve conducting an isostatic pressing study.

The other testing completed to date is the One Dimensional Time-to-Explosion test, which is an isothermal stability test.[3] The new formulations looked very similar to RX-26-AF in this test.

## Future Work

Once we have scaled-up our formulations, and determined those which press the best, we will proceed to determine the shock initiability of these materials. The DOE criteria for shock initiability of an IHE is that the material be no more sensitive than Explosive D (ammonium picrate) in the large scale gap test. We plan to use the wedge test to determine the shock threshold, as it gives more information than the gap test.[3] We have already machined parts of Explosive D for the wedge test, to test as the baseline. These tests will be done once the gun in our new High Explosives Application Facility (HEAF) is operational.

Based on the results of the above, we will hopefully be able to select two or three materials which will be subjected to further safety and performance testing. One formulation will then be selected for larger-scale performance and vulnerability testing (e.g. cylinder test for equation of state, Susan test, bullet test, etc).

## Conclusion

We are developing a family of new explosives, which we expect will significantly exceed the performance of current IHEs. This new family is also expected to pass the IHE criteria, as set forth by the DOE. The new formulations will include TATB, HMX, and high density plasticized binders. Current work has produced several candidates which look promising; up-to-date results will be given during the presentation at the ICT Annual Conference.

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1. H. C. Hornig and R. R. McGuire, Preliminary Development and Characterization of a TATB/HMX Plastic Bonded Explosive, Lawrence Livermore National Laboratory, University of California, UCID-18534, January 1980.

2. Estane 5702-F1 is the trade name for a poly(urethane-ester-MDI) manufactured by Shell Chemical. Kel-F 800 is the trade name for a vinylidine fluoride-chlorotrifluoroethylene copolymer manufactured by 3M. Kraton G-1650 is the trade name for a poly(styrene-ethylene-butylene) block copolymer manufactured by Shell Chemical. Viton A is the trade name for a vinylidine fluoride-hexafluoropropylene copolymer manufactured by DuPont.

3. K. J. Scribner, E. von Holtz, and R. L. Simpson, High-Performance, Extrusion-Cast Explosives with Low Sensitivity: Interim Report No. 2, Lawrence Livermore National Laboratory, University of California, UCRL-53890, January 1989. A brief discussion of the Susan, Rifle Bullet, One-Dimensional Time-to—Explosion (ODTX), NOL Large Scale Gap, and Wedge tests can be found in Appendix B. A portion of this appendix is attached for reference.

4. R. L. Simpson, F. H. Helm, P. C. Crawford, and J. W. Kury, Particle Size Effects in the Initiation of Explosives Containing Reactive and Non-Reactive Continuous Phases, Proceedings of the Ninth Symposium (International) on Detonation, Portland, OR, Aug. 27-Sept. 1, 1989.

5. M. Cowperthwaite and W. H. Zwisler, User's Guide for the Tiger Computer Program, Stanford Research Institute, Menlo Park, California, August 1974.

## APPENDIX B. BRIEF DEFINITIONS OF STANDARD TESTS[B1]

### Susan Test

The Susan test is a projectile-impact test designed to assess the relative sensitivity of an explosive under field conditions of impact. An explosive test sample weighing about 400 grams is loaded into a Susan projectile (Fig. B-1) and gun-fired at the desired velocity at an armor-plate target. The resulting overpressure from the impact-induced reaction is measured using pressure gauges about 3 meters from the point of impact. To show the results graphically, the equivalent mass of TNT (the amount of TNT required to give the observed overpressure if detonated in the Susan test geometry) is plotted as a function of projectile velocity.

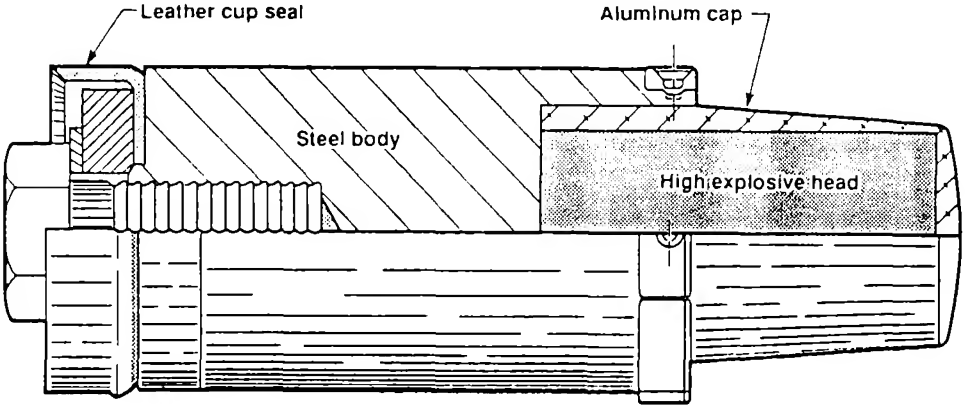


**Fig. B-1. Scale drawing of the Susan projectile.**
**The HE head is 102 mm long and 51 mm in diameter.**

### Rifle Bullet Test

The Pantex DOE plant conducts a standard rifle-bullet test. The target in this test is a 5.1-cm-dia. x 5.8-cm-long billet confined in a 2-in. schedule 40 seamless steel pipe nipple. One end of the pipe is closed by a 7.6-cm-square x 0.32-cm-thick cold-rolled steel plate that has been tack-welded in place. The center of this plate is the target for the projectile. The other end is closed with a standard threaded-pipe cap filled with a stiff sponge material that pushes the billet so that it maintains contact with the target plate (Fig. B-2).

The projectile is a 30-caliber copper-jacketed bullet. Pantex uses military match ammunition to obtain consistency. The muzzle velocity of every round is measured; the range is 823-887 m/s. Most of the time, the projectile stops in the explosive.

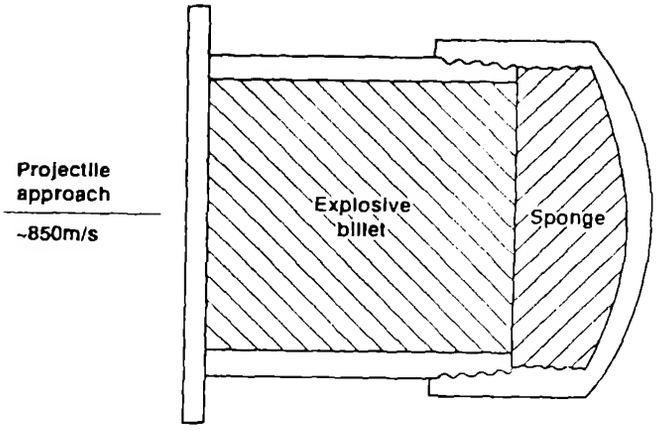


**Fig. B-2. Pantex rifle-bullet test setup.**

### One-Dimensional Time-to-Explosion (ODTX) Test[B2]

In the LLNL One-Dimensional Time-to-Explosion (ODTX) test, 2.2-g samples (12.7-mm-dia. spheres) are placed between two preheated anvils (76.2 mm dia. x 50.8 mm high) and sealed to confine the reaction-product gases. The anvils are heated electrically; the temperature is feedback-controlled using thermocouple transducers. Times to explosion are measured as a function of temperature. Critical temperatures are defined as the asymptotes of the plots of In t vs. 1/T, where t = time and T = temperature.

### NOL Large-Scale Gap Test[B4]

The gap-test data are indicative of the shock sensitivity of an explosive. The values are reported as the thickness of an inert spacer material that has a 50% probability of allowing detonation when placed between the test explosive and a standard detonating charge. In general, the larger the spacer gap, the more shock-sensitive the HE. The values, however, depend on test size and geometry and on the sample (the particular lot, its method of preparation, its density, and percent voids). Gap test results, therefore, are only approximate indications of relative shock sensitivity. See Fig. B-3.

### Wedge Test[B5]

Wedge tests are used to determine the shock-compression behavior of energetic materials as well as the distance a non-reaction-supported shock wave travels through an explosive before it transitions to detonation. Figure B-4 shows the experimental configuration along with the interpretation of a typical data set. A high-velocity flyer plate impacts a target in which an array of piezoelectric shock transducers are embedded at different depths in the explosive sample. The first linear region in the Position-vs.-Time curve represents the shock Hugoniot of the material and is a line on the equation of state surface. Using the measured shock velocity, along with the flyer velocity and its known Hugoniot, in the Rankine-Hugoniot shock jump equations enables the shock-compression data of the sample to be determined. This information includes the actual pressure of the shock wave.

It is assumed that any contribution to the shock pressure from chemical reaction (hence, to the shock velocity) is negligible before the detonation transition. In the shock-to-detonation region, reaction rates build rapidly near the wave front, and the shock velocity becomes that of full detonation. The intersection of the two linear portions of the curve in Fig. B-4(b) is taken as the run distance in the explosive. These distances are a measure of a material's shock-initiation sensitivity. It has been found empirically that a log-log plot of run distance vs. shock pressure ("Pop-plot") is approximately linear.

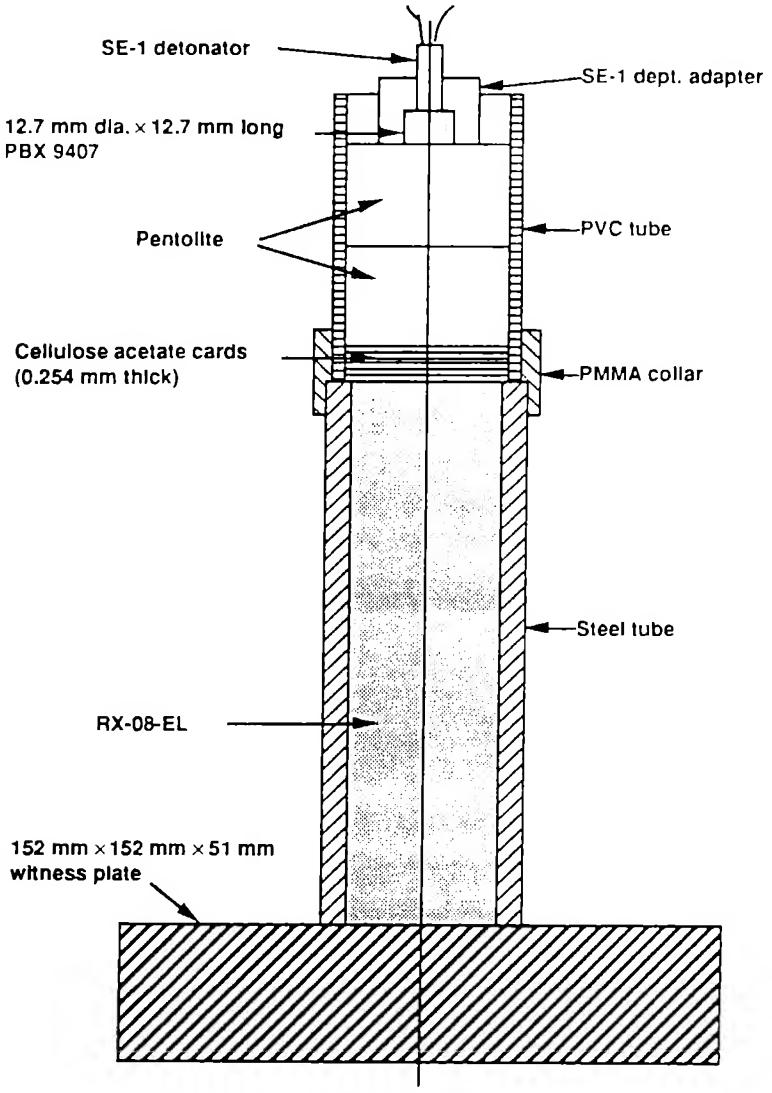


Figure B-3. NOL large-scale gap test setup.

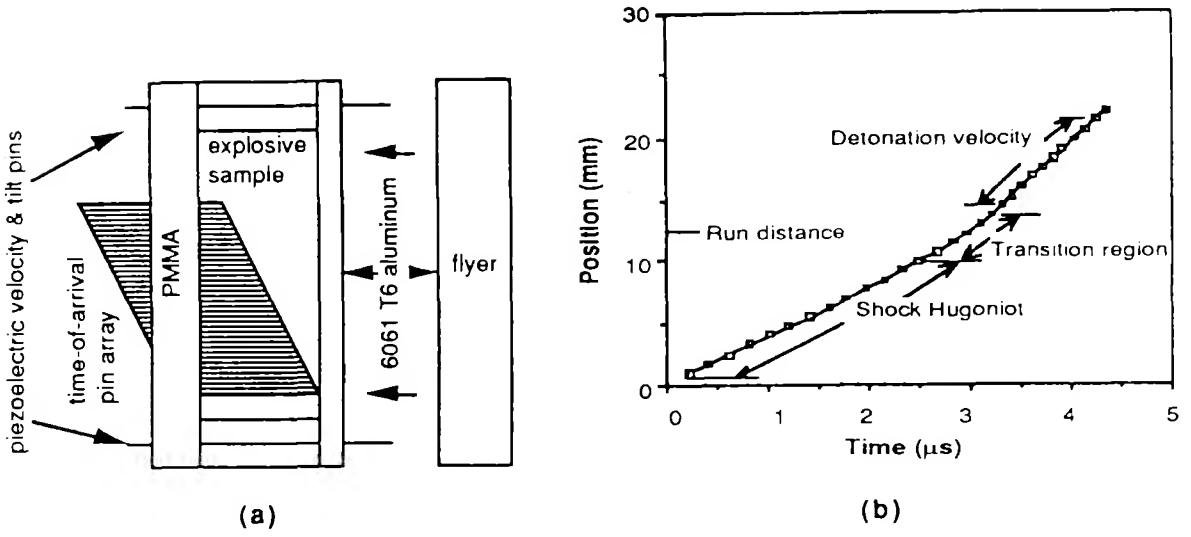


**Figure B-4. (a) Wedge test configuration; (b) interpretation of data.**

### Cylinder-Test Measurements of Explosive Energy

The cylinder test gives a measure of the hydrodynamic performance of an explosive. The test geometry is based on a constant volume of HE. The test system consists of an explosive charge 25 mm in diameter and 310 mm long in a tightly-fitting copper tube with a wall 2.6 mm thick. The charge is initiated at one end. The radial motion of the cylinder wall is measured at about 200 mm from the initiated end using a streak camera. The camera records are reduced to provide detailed radius-time information.

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B3. R. R. Fyfe, *A Screening Test for Low-Velocity Detonation in thin Films of Liquid Explosives,* Lawrence Livermore National Laboratory, Livermore, Calif., UCRL-75120 (1973).

B4. J. Taylor, *Detonation in Condensed Explosives* (Clarendon Press, Oxford, 1952).

B5. T. Gibbs and A. Popolato, *LASL Explosives Property Data* (University of California Press, Berkeley, 1980), p. 293.